INTRODUCTION

There has been extensive progress made in recent years in research towards the development of analytic statistical-mechanical equations of state applicable for process design calculations (Alem and Mansoori, 1984). However, cubic equations of state are still widely used in chemical engineering practice for the calculation and prediction of properties of fluids and fluid mixtures (Renon, 1983). These equations of state are generally modifications of the van der Waals equation of state,

\[ P = \frac{RT}{v-b} - \frac{a}{v^2} \]  

(1)

which was proposed by van der Waals in 1873. According to van der Waals, the extension of this equation of state to mixtures requires replacement of \( a \) and \( b \) by the following composition-dependent expressions:

\[ a = \sum_i \sum_j x_i x_j a_{ij} \]  

(2)

\[ b = \sum_i \sum_j x_i x_j b_{ij}. \]  

(3)

Equations (2) and (3) are called the van der Waals mixing rules. In these equations, \( a_{ij} \) and \( b_{ij} \) \((i = j)\) are parameters corresponding to pure component \((i)\) while \( a_{ij} \) and \( b_{ij} \) \((i \neq j)\) are called the unlike-interaction parameters. It is customary to relate the unlike-interaction parameters to the pure-component parameters by the following expression:

\[ a_{ij} = (1 - k_{ij}) (a_{ii} a_{jj})^{1/2} \]  

(4)

\[ b_{ij} = (b_{ii} + b_{jj})/2. \]  

(5)

In eq. (4), \( k_{ij} \) is a fitting parameter which is known as the coupling parameter. With eq. (5) substituted in eq. (3), the expression for \( b \) will reduce to the following one-summation form:

\[ b = \sum_i x_i b_{ii}. \]  

(3.1)

Extensive research on equations of state have indicated that the van der Waals equation of state is not accurate enough for the prediction of properties of compressed gases and liquids (Rowlinson and Swinton, 1982). This deficiency of the van der Waals equation of state has initiated a great deal of research on the development of other equations of state, through the use of principles of statistical mechanics or by empirical or semi-empirical means. The majority of equations of state used in chemical engineering practice are of the second category and are mostly cubic in the volume, like the van der Waals equation of state itself, but contain other forms of the temperature and volume dependencies. One such equation of state which has a simple form is the Redlich-Kwong equation of state (Redlich and Kwong, 1949):

\[ P = \frac{RT}{v-b} - \frac{a}{v^{1/2} (v-b)}. \]  

(6)

This equation of state has found widespread applications in chemical engineering calculations. We would also like to mention that there exist a large number of more sophisticated empirical versions of the van der Waals and Redlich-Kwong modifications. Of this category of equations of state, the Peng-Robinson equation of state (Peng and Robinson, 1976)

\[ P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} \]  

(7)

\[ a(T) = a(T_c) \left\{ 1 + \kappa (1 - T_c^{-1/2})^2 \right\} \]  

(8)

\[ a(T_c) = 0.45724 \frac{RT_c}{P_c} \]  

(8.1)

\[ \kappa = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \]  

(9)

\[ b = 0.0778 RT_c/P_c \]  

(10)

is widely used for thermodynamic property calculations.

While there has been extensive activity in the development of new and more accurate empirical cubic equations of state, there has been little attention to the fact that the van der Waals mixing rules are used
words, for the extension of applicability of a cubic
equation of state it is not generally correct to use eqs (2)
and (3.1) as the mixing rules without attention to the
algebraic form of the equation of state. In the present
paper we introduce a new concept for the development
of mixing rules for cubic equations of state in the spirit
of the van der Waals mixing rules. This concept is
based on statistical-mechanical arguments and the fact
that the van der Waals mixing rules are for constants of
an equation of state and not for any thermodynamic
state function which may appear in an equation of
state. The resulting mixing rules for the 
Redlich–Kwong equation of state, which is a simple
modification of the van der Waals equation of state,
and for the Peng–Robinson equation of state, which is
an advanced modification of the van der Waals
equation of state, are tested through prediction of
solubility of heavy solids in supercritical fluids.

THEORY OF THE VAN DER WAALS MIXING RULES

Leland and co-workers (1968a, b, 1969) were able to
re-derive the van der Waals mixing rules with the use
of statistical-mechanical theory of radial distribution
functions. According to these investigators, for a fluid
mixture with a pair intermolecular potential energy
function between molecules of the mixture in the form
\[ u_{ij}(r) = \varepsilon_{ij} f(r/\sigma_{ij}) \] (11)
the following mixing rules will be derived:
\[ \sigma^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \] (12)
\[ \varepsilon^3 = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^3. \] (13)

In these equations, \( \varepsilon_{ij} \) is the interaction energy
parameter between molecules \( i \) and \( j \) and \( \sigma_{ij} \) is the
intermolecular interaction distance between the
two molecules. Coefficients \( a \) and \( b \) of the van der
Waals equation of state are proportional to \( \varepsilon \) and \( \sigma \)
according to the following expressions:
\[ a = 1.1250 RT_v \varepsilon v_c \propto N_o \varepsilon \sigma^3 \] (14)
\[ b = 0.3333 v_c \propto N_o \sigma^3. \] (15)

We can see that eqs (12) and (13) are identical with
eqs [2] and [3], respectively. Statistical-mechanical
arguments used in deriving eqs (12) and (13) dictate the
following guidelines in using the van der Waals mixing
rules:

1. The van der Waals mixing rules are for constants of
an equation of state.

2. Equation (12) is a mixing rule for the molecular
volume, and eq. (13) is a mixing rule for (molecular
volume) \( \times \) (molecular energy). It happens that \( b \)
and \( a \) of the van der Waals equation of state are
proportional to molecular volume and (molecular
volume) \( \times \) (molecular energy), respectively, and, as
a result, these mixing rules are used in the form
which was originally proposed by van der Waals.

3. Knowing that \( \sigma_{ij} \) (for \( i \neq j \)), the unlike-interaction
diameter, for spherical molecules, is equal to
\[ \sigma_{ij} = (\sigma_i + \sigma_j)/2. \] (16)

This gives the following expression for \( b_{ij} \) of
spherical molecules:
\[ b_{ij} = [(b_i^{1/3} + b_j^{1/3})/2]^3. \] (17)

Then for non-spherical molecules the expression for
\( b_{ij} \) will be
\[ b_{ij} = (1 - l_{ij}][(b_i^{1/3} + b_j^{1/3})]^3. \] (18)

With the use of these guidelines, we now derive the
van der Waals mixing rules for the two representative
equations of state. A similar procedure can be used for
deriving the van der Waals mixing rules for other
equations of state.

Mixing rules for the Redlich–Kwong equation of state

The Redlich–Kwong equation of state, eq. (6), can
be written in the following form:
\[ Z = \frac{pV}{RT} = \frac{v}{v - b} - \frac{a}{RT^{1.5}(v + b)}. \] (19)

In this equation of state, \( b \) has the dimension of a molar
volume,
\[ b = 0.26 v_c \propto N_o \sigma^3. \]

Then the mixing rule for \( b \) will be the same as that for
the first van der Waals mixing rule, eq. (3). However,
the mixing rule for \( a \) will be different from the second
van der Waals mixing rule. Parameter \( a \) appearing in
the Redlich–Kwong equation of state has the dimensions
of \( R^{-1/2} \) (molecular energy)^{3/2} (molecular
volume), that is,
\[ a = 1.2828 R T_v^{1.5} v_c \propto N_o \sigma^3. \]

As a result, the second van der Waals mixing rule, eq.
(13), cannot be used directly for the \( a \) parameter of the
Redlich–Kwong equation of state. However, since
\( (R^{1/2} a b^{1/2}) \) has the dimensions of (molecular energy)
\( \times \) (molecular volume), the second van der Waals
mixing rule, eq. (13), can be written for this term.
Finally, the van der Waals mixing rules for the
Redlich–Kwong equation of state will be in the
following form:
\[ a = \left\{ \sum_i \sum_j x_i x_j a_{ij}^{1/3} b_{ij}^{1/3} \right\}^{1.5} \left( \sum_i \sum_j x_i x_j b_{ij} \right)^{1/2} \] (20)
\[ b = \sum_i \sum_j x_i x_j b_{ij}. \] (3)

These mixing rules, when combined with the
Redlich–Kwong equation of state, will constitute the
Redlich–Kwong equation of state for mixtures, con-
sistent with the statistical-mechanical basis of the van
der Waals mixing rules.

Mixing rules for the Peng–Robinson equation of state

In order to separate thermodynamic variables from
constants of the Peng–Robinson equation of state, we will insert eqs (8) and (9) into eq. (7) and we will write it in the following form:

\[
Z = \frac{v}{v - b} - \frac{a/RT + d - 2 \sqrt{(ad/RT)} - (v + b) + (b/v)(v - b)}{(v + b) + (b/v)(v - b)}
\]  
(21)

where \(a = a(T_c)(1 + \kappa)^2\) and \(d = a(T_c)\kappa^2/RT_c\).

This form of the Peng–Robinson equation of state suggests that there exist three independent constants in this equation of state: \(a, b\) and \(d\). Now, following the prescribed guidelines for the van der Waals mixing rules, the mixing rules for \(a, b\) and \(d\) of the Peng–Robinson equation of state will be

\[
a = \sum_{i} \sum_{j} x_i x_j a_{ij}
\]
(22)

\[
h = \sum_{i} \sum_{j} x_i x_j b_{ij}
\]
(23)

\[
d = \sum_{i} \sum_{j} x_i x_j d_{ij}
\]
(24)

with the following interaction parameters:

\[
a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2}
\]
(25)

\[
b_{ij} = (1 - l_{ij}) \left\{ \left( b_i^{1/3} + b_j^{1/3} \right)/2 \right\}^3
\]
(26)

\[
d_{ij} = (1 - m_{ij}) \left\{ \left( d_i^{1/3} + d_j^{1/3} \right)/2 \right\}^2.
\]
(27)

These mixing rules, when joined with the Peng–Robinson equation of state, eq. (7), will constitute the Peng–Robinson equation of state of a mixture, consistent with the statistical-mechanical basis of the van der Waals mixing rules.

**APPLICATION FOR SUPERCRITICAL FLUID EXTRACTION MODELLING**

A serious test of mixture equations of state is shown to be their application for the prediction of solubility of heavy solutes in supercritical fluids (Mansoori and Ely, 1985). In the present paper, we apply the van der Waals, the Redlich–Kwong and the Peng–Robinson equations of state for supercritical fluid extraction of solids and study the effect of choosing different mixing rules for predicting the solubility of solids in supercritical fluids.

The solubility of a condensed phase, \(y_2\), in a vapour phase at supercritical conditions can be defined as:

\[
y_2 = \left( \frac{P_2^{sat}/P}{\phi_2^{sat}} \right) \exp \left\{ \int_{P_2}^{P} \left( \frac{v_2^{sat}/RT}{P} \right) dP \right\}
\]
(28)

where \(\phi_2^{sat}\) is the fugacity coefficient of the condensed phase at the saturation pressure \(P_2^{sat}\), and \(\phi_2\) is the vapour phase fugacity at pressure \(P\). Provided we assume that \(v_2^{sat}\) is independent of pressure, the above expression is converted to the following form:

\[
y_2 = \left( \frac{P_2^{sat}/P}{\phi_2} \right) \exp \left\{ v_2^{sat} (P - P_2^{sat})/RT \right\}.
\]
(29)

In order to calculate solubility from eq. (29), we need to choose an expression for the fugacity coefficient. Generally, for calculation of a fugacity coefficient an equation of state with appropriate mixing rules is used in the following expression (Prausnitz, 1969):

\[
RT \ln \phi_i = \int_{P_i}^{P} \left[ \frac{(\partial P/\partial n_i)_{T_i, v, n_{i-1}}}{(RT^2)} \right] dV
\]
(30)

where \(Z = P_0/RT\).

In the case of the van der Waals equation of state, eq. (1), with eqs (2) and (3) as the mixing rules, the following expression for the fugacity coefficient of a solute in a supercritical gas will be derived:

\[
\phi_i = \frac{RT/\gamma}{(v-b)/P} \exp \left\{ \frac{(b+2\Sigma x_j b_{ij})}{(v-b)} \right\}
- \frac{1}{2} \Sigma x_j d_{ij}/vRT
- \Sigma x_j a_{ij}/vRT
\]
(31)

For the Redlich–Kwong equation of state, with eqs (2) and (3) as its mixing rules (as customary in the literature), the following expression for the fugacity coefficient is obtained:

\[
\ln \phi_i = \ln \left( \frac{\gamma}{(v-b)} \right) + \frac{(2\Sigma x_j b_{ij} - b)}{(v-b)} - \ln \frac{\gamma}{(v-b)}
+ a(2\Sigma x_j b_{ij} - b)/(b^2RT^{1.5}) \ln \left( \frac{(v+b)/v}{(v+b)/v} \right)
- b/(v+b) - 2\Sigma x_j a_{ij}/(bRT^{1.5})
\times \ln \left( \frac{(v+b)/v}{(v+b)/v} \right).
\]
(32)

Now with the use of the correct version of the van der Waals mixing rules, eqs (22) and (24), in the Redlich–Kwong equation of state, the fugacity coefficient will assume the following form:

\[
\ln \phi_i = \ln \left( \frac{\gamma}{(v-b)} \right) + \frac{(2\Sigma x_j b_{ij} - b)}{(v-b)} - \ln \frac{\gamma}{(v-b)}
+ a(2\Sigma x_j b_{ij} - b)/(b^2RT^{1.5}) \ln \left( \frac{(v+b)/v}{(v+b)/v} \right)
- b/(v+b) - \Sigma x_j a_{ij}/(bRT^{1.5})
\times \ln \left( \frac{(v+b)/v}{(v+b)/v} \right).
\]
(33)

where

\[
\alpha = \sum_{i} \sum_{j} x_i x_j a_{ij}^{1/3} b_{ij}^{1/3}.
\]

The fugacity coefficient based on the Peng–Robinson equation of state with eqs (2) and (3) as the mixing rules (as usually derived) has the following form (Kurnik et al., 1981):

\[
\ln \phi_i = \left( 2\Sigma x_j b_{ij} - b \right)/\gamma \left( Z-1 \right) - \ln \left( Z-B \right)
- \left( A/2 \right) \sqrt{2B} \ln \left( 2\Sigma x_j a_{ij}/(2\Sigma x_j b_{ij} - b) \right)
	\times \ln \left( Z + 2\sqrt{2B}/(Z - 2\sqrt{2B}) \right)
\]
(34)

where \(A = aP/R^2T^2\) and \(B = bP/RT\).

With the use of the correct version of the van der Waals mixing rules, eqs (22)–(24), in the Peng–Robinson equation of state, the following expression
for the fugacity coefficient is derived:

\[
\ln \phi_i = \frac{(2 \Sigma x_i b_{ij} - b)}{b} (Z - 1) - \ln (Z - B)
- \frac{4 \sqrt{(RT)}}{a b} (2 \Sigma x_i d_{ij} + 2 R T \Sigma x_i d_{ij}
+ d \Sigma x_i a_{ij} \sqrt{(ad)})/a^* - (2 \Sigma x_i b_{ij} - b)/b
\times \ln \left(\left(\frac{Z + (1 + \sqrt{2}) B}{Z - (1 - \sqrt{2}) B}\right)\right)
\]  

(35)

where

\[a^* = a + RT d - 2 \sqrt{(adRT)} \]

\[A = a^* P/(RT)\]

\[B = b RT/(RT)\].

We now utilize the above expressions for fugacities in order to predict the solubility of solids in supercritical gases at different temperatures and pressures, and compare the results with the experimental data.

RESULTS AND DISCUSSION

In Fig. 1, the solubility of 2,3-dimethyl naphthalene (DMN) in supercritical carbon dioxide is plotted vs. pressure at 308 K along with predictions obtained from the van der Waals equation of state. According to this figure, predictions by the van der Waals equation of state will improve when eq. (3), along with the combining rule, eq. (17), is used as the mixing rule for \(b\) instead of eq. (3.1) as customarily used. This comparison, and similar comparisons reported elsewhere (Mansoori and Ely, 1985) for other solute-solvent systems, establish the superiority of the double-summation mixing rule, eq. (3), for \(b\) over the single-summation expression, eq. (3.1).

In Fig. 2, the same experimental solubility data as in Fig. 1 are compared with predictions using the Redlich–Kwong equation of state. According to this figure, the corrected van der Waals mixing rules for the Redlich–Kwong equation of state, eqs (3) and (20), are clearly superior to the mixing rules which are customarily used, eqs (2) and (3.1), for this equation of state. Similar observations are made for the prediction of solubilities of other solids in supercritical fluids, which are not reported here.

The Peng–Robinson equation of state with its customary mixing rules, eqs (2) and (3), is widely used for predicting the solubility of heavy solutes in supercritical gases and for petroleum reservoir fluid-phase equilibrium calculations (Firoozabadi et al., 1978; Katz and Firoozabadi, 1978; Kurnik et al., 1981). In Fig. 3 the same experimental solubility data as in Figs 1 and 2 are compared with the predictions using the Peng–Robinson equation of state with its original mixing rules and with its corrected van der Waals mixing rules. According to this figure, the corrected
van der Waals mixing rules of the Peng–Robinson equation of state apparently do not improve solubility predictions over the original mixing rules. However, variation of solubility vs. pressure for the new mixing rules is more consistent with the experimental data than the old mixing rules. Also considering the fact that the new mixing rules for the Peng–Robinson equation of state contain three adjustable parameters ($k_{ij}, l_{ij}$ and $m_{ij}$) whereas the old mixing rules contain only two adjustable parameters ($k_{ij}$ and $l_{ij}$) makes the new mixing rules more attractive. A demonstration of the superiority of the new mixing rules for the Peng–Robinson equation of state is shown here in Figs 4–9. According to these figures, when the unlike-interaction adjustable parameters of the mixing rules are fitted to the experimental data, the Peng–Robinson equation of state with the corrected van der Waals mixing rules can predict solubility of heavy solids in supercritical fluid more accurately than with the original mixing rules over different ranges of temperature and pressure and for different solutes and supercritical solvents.
Fig. 6. Solubility of 2,3-dimethyl naphthalene (DMN) in supercritical ethylene as calculated by the Peng-Robinson equation of state with eqs (2) and (3) as the mixing rules and compared with the experimental data.

Fig. 7. Solubility of 2,3-dimethyl naphthalene in supercritical ethylene as calculated by the Peng–Robinson equation of state with eqs (22)–(24) as the mixing rules and compared with the experimental data.

Fig. 8. Solubility of 2,6-dimethyl naphthalene (DMN) in carbon dioxide as calculated by the Peng–Robinson equation of state with eqs (2) and (3) as the mixing rules and compared with the experimental data.

Fig. 9. Solubility of 2,6-dimethyl naphthalene (DMN) in supercritical carbon dioxide as calculated by the Peng–Robinson equation of state with eqs (22)–(24) as the mixing rules and compared with the experimental data.
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NOTATION

A, B Variable in the Peng–Robinson equation of state
a, b parameter in the equation of state
d parameter in the Peng–Robinson equation of state
k_ij binary interaction parameter
l_ij binary interaction parameters in the Peng–Robinson equation of state
m_ij binary interaction parameters in the Peng–Robinson equation of state
N_o Avogadro’s number
P pressure, Bar
R universal gas constant
T temperature, K
u intermolecular potential energy function
v molar volume, cm^3/mol
y gas phase mole fraction
Z compressibility factor

Greek letters

\( \varepsilon \) interaction energy parameter
\( \omega \) acentric factor
\( \phi \) fugacity coefficient
\( \sigma \) intermolecular length parameter

Subscripts

i, j component identifiers
2 solute
c critical property

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T. Y. KWAK and G. A. MANSOORI
VAN DER WAALS MIXING RULES FOR CUBIC EQUATIONS OF STATE.
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